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The optical properties of four Tm^{3+} ion - organic ligand chelat complexes in a poly(methyl methacrylate) matrix were studied. These materials are interesting for potential applications of optical hole-burning frequency and time-domain storage and processing. Optical absorption, steady state and time-resolved photoluminescence, and spectral hole-burning at the transition between $^3H_6(1)$ and $^3H_4(1)$ crystal-field levels were studied at temperatures between 1.4 and 300 K. The heterodyne grating-generated scan interferometric technique has been demonstrated for the real time detection of the femtosecond data signal.

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Materials for High - Temperature Spectral Hole-Burning Optical Storage

October 8, 1999

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Mr. G. Bai, 1997

Progress of the spectral hole-burning technology for multicolor optical storage and signal processing critically depends on success in search and synthesis of new materials. Our research is aimed mostly on potentially useful materials for persistent optical storage. To characterize and compare different hole burning materials we determined material parameters such as cross section of optical transition, quantum yield of hole burning, inhomogeneous and homogeneous broadening, and hole lifetime. The temperature dependence of these parameters is important for understanding their basic science and high temperature applications. Another direction of our research is directed to the sophistication of the previously developed interferometric amplitude crosscorrelation technique, which has capability of ultrafast single shot echo readout.

The progress was achieved in areas of upgrading of laboratory equipment, materials, and research.

1. Laboratory.

Prof. A. Gorokhovsky has received a full time faculty position at College of Staten Island of CUNY beginning September 1996. For this reason, the laser hole burning equipment was relocated from CCNY to CSI and set up to characterize materials. The room for the laboratory was renovated including purchase and installation of a new Newport vibration isolated optical table and air-conditioning system. Major laser equipment including Innova 310 Argon Ion Laser System and 899-29 Autoscan II Ti:S single-frequency ring laser was installed. Detection system including lock-in amplifier, monochromator, GaAs cooled photomultiplier, and computer data acquisition board was upgraded and installed. A new Oxford Instruments variable temperature

helium cryostat has been purchased and helium pump and pumping line have been installed. This unit allows us to perform measurements at temperatures from 1.4 to 300 K. In addition, key spectroscopic equipment, including Perkin Elmer Lamda 900 spectrophotometer has been purchased and set up at CSI to determine the major spectroscopic parameters of the materials under investigation. Part of the research project related to the interoferometric crosscorrelation technique for ultrafast photon echo detection was continued at IUSL/CCNY.

2. Materials.

New Tm^{3+} ion - organic ligand complexes in poly(methyl methacrylate (Prof. Y. Okamoto, Polytechnic University, Brooklyn, NY), have been produced for the study. Samples under investigation were four Tm^{3+} ion β-diketone tris chelate complexes. Chelates where prepared using thulium chloride ($TmCl_3 \bullet 6H_2O$) with thenoyltrifluoroacetylacetone (TTFA), 1,1,1-trifluoro-2,4-pentanedione (TFD), 1-phenyl-1,3-butanedione (PBD), and 1,3-diphenyl-1,3-propanedione (DBM) ligands. The concentration of the Tm3+ ion in the samples was determined on the basis of input chemical concentrations and found to be 0.35, 0.14, 0.32, and 0.2 mol % for $Tm^{3+}(TFD)_3$, $Tm^{3+}(TTFA)_3$, $Tm^{3+}(PBD)_3$, and $Tm^{3+}(DBM)_3$ complexes, respectively. Physically, the samples appeared to be transparent slightly yellow colored cylinders, having diameters of 8 - 10 mm and lengths of 15-20 mm.

3. Research.

Our research focused on a series of measurements which included absorption and fluorescence spectra, electronic state lifetimes, hole burning kinetics and quantum yield, spectra

and hole lifetimes of selected materials in broad temperature region 1.4 - 300 K, and ultra sensitive photon echo signals detection technique on femtosecond time scale. The following highlights the salient aspects of the work.

3.1 Rare earth doped polymers.

We studied spectral hole-burning at 0-0 transition between $^3H_6(1)$ and $^3H_4(1)$ crystal-field levels at 795 nm of Tm^{3+} ion using a single frequency Ti:Sapphire laser. The inhomogeneous broadening of this transition was found to be between 4300 and 2800 GHz for all four samples studied. The long-lived holes were observed in all materials. The holes show no visible recovery at 1.4 K over the experimental time of 10 hours. The maximum measured hole depth was about 50 %. . Kinetics of the spectral hole growth were recorded at time scale 10^{-2} - 10^4 s. They show dispersive behavior associated with distribution of the hole burning efficiency. The hole-burning mechanism appears to be a photoinduced rearrangement of the local structure of the Tm^{3+} ion surrounding. Some critical parameters of hole-burning, including absorption peak cross section, quantum efficiency, and maximum hole-burning and annealing temperatures were determine and compared for all samples.

The holewidth dependence on burning time at different intensities was used to determine the conditions for the weak burning intensity regime. The "true" holewidth for different materials was found to be Γ_{hole} = 180-360 MHz by using the zero limit of the burning intensity and of the exposure time. This "true" holewidth reflects optical dephasing caused by the interaction with phonons, tunneling systems, and surrounding spins (in the time scale of the excited state lifetime), as well as the slower spectral diffusion. Separation of these effects requires fast time-

resolved measurements. The temperature dependence of the holewidth was measured at temperatures between 1.4 and 16 K. A weak power law temperature dependence $\Gamma_{hole} \propto T^n$ with n = 1 - 1.6 was observed for all materials. A similar dependence of the homogeneous line broadening with n = 1 - 2 were observed in many doped glasses and polymers, and explained as to be due to the interaction between the optical transition in the impurity ion and the low frequency excitations (quasilocal vibrations and tunneling systems) of the amorphous matrix.

To verify the ability of the materials under investigation to store a number of spectral holes, we performed hole burning at different wavelengths over the inhomogeneous broadened absorption band. A number of holes were observed over the full inhomogeneously broadened band of the $^3H_6(1) \rightarrow {}^3H_4$ (1) transition, i.e. in the bandwidth of 100 cm^{-1}, or 3000 GHz. For example, a set of eight consecutive holes burned over a region of 8 GHz. No visible laser - induced filling or broadening was detected on first "test" hole over the time of burning of the other seven holes. We expect the same behavior over the full inhomogeneously broadened absorption band. Data on the inhomogeneous broadening and the holewidth for all of the materials studied are presented in the Table.

Table. Holewidths and inhomogeneous widths of the $^3H_4$ (1) $\leftarrow$ $^3H_6$ (1) transition of Tm^{3+} chelates in PMMA.

Parameters	$Tm(TTFA)_3$	$Tm(TFD)_3$	$Tm(PBD)_3$	$Tm(DBM)_3$
Γ_{inh} (GHz)	3000	4300	2800	2500
Γ_{hole} (MHz)	220	230	360	180
$\Gamma_{inh} / \Gamma_{hole}$	1.4×10^4	1.9×10^4	0.8×10^4	1.4×10^4

3.2 Femtosecond photon echo detection.

In a parallel effort, time resolved research was performed in writing and retrieval of the femtosecond accumulated photon echo. The photon echo (PE) spectra were measured, and analyzed in free-base octaethilporphyn in polystyrene at 1.4 K to minimize spectral distortion (deviation in shape and FWHM compare to the original pulse spectrum) to improve a time resolution of the crosscorrelation technique and receive a shorter amplitude correlation time of the PE signal from hole-burning material.

Spectral holograms were written by CPM laser at two wavelengths, 620 nm, or 616 nm, and studied in multi- and single shot readout mode. For wavelength of 620 nm, the PE spectrum consists of two bands. The most intensive band at 622 nm is more the twice narrower (FWHM $\approx$ 2.5 nm) than readout pulses spectrum. As a result, a correlation time of the PE signal became twice longer. The PE spectrum changed dramatically when writing and readout were performed at another wavelength of 616 nm. The spectrum (FWHM $\approx$ 4 nm) became smooth and only about 10 % narrower than the readout pulse spectrum. The PE efficiency at 620 nm was about twice more than at 616 nm writing wavelength because of the influence of the phonon wings in the short-wavelength region of the absorption band.

Detection of ultrashort time-domain signals requires receiver systems such as streak camera and second harmonic generation methods. A new single-shot detection of ultrashort time-domain signals was developed for optical data storage as well as for time-domain optical communications. This new method converts the time propagation of pulses into a corresponding coherence-domain interference pattern that permits the simultaneous registration of reflections by use of a diffraction grating and a linear CCD array. An accumulated photon echo read-out speed

as fast as 27 Terabit per second was demonstrated in the past using this single-shot crosscorrelation method for a femtosecond four-pulse packet stored by spectral hole burning in a octaethylporphine-doped polystyrene sample.

Recently, the heterodyne grating- generated scan interferometric technique has been demonstrated for the real-time detection of the femtosecond data signals. Heterodyne detection is performed using the Doppler frequency shift that results from the moving of the reflection diffraction grating in the direction of the grating dispersion with constant speed **v**. The projections of the speed vector **v** on the direction of the reference (signal) beam are $\mathbf{v}_{r,s} = \pm \mathbf{v}$ **sin**α, where $\pm \alpha$ is the angle between the reference (r) (signal (s)) beams and the normal to the DG. The Doppler frequency shift between diffracted reference and signal beams is given by:

$$\Delta f_D = 2\ v\ f\ \sin\alpha\ /c = 2\ v\ \sin\alpha\ /\lambda = 2v\ /\ p, \qquad (1)$$

where **p** is the space between DG grooves, **f** and λ are light frequency and wavelength, respectively. For our setup **v** = 2.5 mm/s and **p** = 1/1200 mm, than Δf_D = 6 KHz.

The output interference signal is temporal modulated at a frequency equal of Δf_D . The signal from the interferometer is focusing to a scanning mirror, which is mounted upon a rotating galvanometer. The reflected beam is directed to a photodiode connected to a lock-in amplifier and a computer. The photodiode signal magnitude recorded as a function of the scanning mirror angle position profiles the reflectance of the sample as well as femtosecond pulse train.

We developed a new system, which is using an acousto-optical deflector to scan the beam through the slit. The acousto-optical modulator and lock-in amplifier are proposed for heterodyne detection. For this system a complete data acquisition is about 100 μs which is much faster than other methods.

Several features of this technique are attractive for the commercial applications. First, this setup can be fiber-optic based, allowing inexpensive integration with optical data storage systems and telecommunications networks. Second, this system can performe at high speed, allowing data readout speed as fast as 0.1 Gbit/s.

4. Publications and presentations.

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Abstract.

The optical properties of four Tm^{3+} ion - organic ligand chelat complexes in a poly(methyl methacrylate) matrix were studied. These materials are interesting for potential applications of optical hole-burning frequency and time-domain storage and processing. Optical absorption, steady state and time-resolved photoluminescence, and spectral hole-burning at the transition between $^3H_6(1)$ and $^3H_4(1)$ crystal-field levels were studied at temperatures between 1.4 and 300 K. The heterodyne grating-generated scan interferometric technique has been demonstrated for the real time detection of the femtosecond data signal.